

4. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

4.1 PRODUCTION

The demand for hydrogen cyanide in the United States during 1992 was 1.2 billion pounds; this demand is projected to grow 3-4% per year up to 1.46 billion pounds in 1997. The demand for hydrogen cyanide increased by 3-4% per year during the period of 1983-92 (CMR 1993). Major producers of hydrogen cyanide are American Cyanamid Co. (Fortier, Louisiana); BP Chemicals (Green Lake, Texas and Lima, Ohio); Ciba-Geigy Corp. (St. Gabriel, Louisiana); Cyanco Co. (Winnemucca, Nevada); Cytec Industries (Avondale, Louisiana); Degussa Corp. (Theodora, Alabama); Dow Chemical (Freeport, Texas); DuPont (Memphis, Tennessee; Beaumont, Texas; Orange, Texas; and Victoria, Texas); FMC Corporation (Green River, Wyoming); Monsanto (Alvin, Texas and Chocolate Bayou, Texas); Rh&e-Poulenc Ag Company (Institute, West Virginia); Rhom and Haas Texas Inc. (Deer Park, Texas); and Sterling Chemicals, Inc. (Texas City, Texas) (CMR 1993; SRI 1995). The combined annual production capacity of these plants is approximately 1.7 billion pounds (CMR 1993; SRI 1995). Producers of hydrogen cyanide in the United States having maximum on-site amounts greater than 100,000 pounds are: American Cyanamid Co. (Louisiana), BP Chemicals (Texas and Ohio), Ciba-Geigy Corp. (Louisiana), Degussa Corp. (Alabama), Du Pont Chemical Company (two Texas sites), and Monsanto (Texas) (TR193 1995).

As of January 1994, the following companies produced other cyanide compounds in the United States (HSDB 1996; SRI 1994, 1995):

ammonium thiocyanate:	Witco Corporation, Taft, Louisiana; Akzo America, Inc., Janesville, Wisconsin; and The Proctor and Gamble Company, Phillipsburg, New Jersey;
cyanogen:	Matheson Gas Products, Inc., Gloucester, Massachusetts;
potassium cyanide:	Du Pont Chemical Company, Memphis, Tennessee; and Hampshire Chemical Corporation, Nashua, New Hampshire; and
potassium silver cyanide:	Engelhard Corporation, Union, New Jersey; and American Chemical & Refining Company, Waterbury, Connecticut.

Facilities producing sodium cyanide and their annual capacity (in millions of pounds) include: Cyanco Co., Winnemucca, Nevada (28); Degussa Corporation, Theodore, Alabama (60); Du Pont Chemical Company, Memphis, Tennessee (250) and Texas City, Texas (100); and FMC Corporation, Green River, Wyoming (60) (SRI 1995).

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Facilities in each state that manufactured or processed hydrogen cyanide in 1992, the range of the maximum amounts stored on site, and the types of production or use activities (e.g., production for sale or on-site use in processing) are shown in Table 4-1 (TRI93 1995). The information in Table 4-1 is derived from the Toxics Release Inventory (TRI). The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. No information is available in the TRI database for other cyanide and thiocyanate compounds in this profile because these compounds are not included under SARA, Title III and, therefore, are not among the chemicals that facilities are required to report (EPA 1993g).

There are two common methods of manufacturing hydrogen cyanide. The first consists of the formation of hydrogen cyanide as a by-product during the synthesis of acrylonitrile from the reaction of propylene and ammonia with air. The second method involves direct synthesis by the reaction of methane and ammonia with air over platinum catalysts (CMR 1993; Curry 1992; Homan 1987). Other methods of production include the dehydration of formamide, and reaction of sodium carbonate with coke-oven gas (Curry 1992; Sittig 1980). The formamide method of production has now been replaced by direct synthesis from methane and ammonia (Homan 1987). Of the total production capacity, direct synthesis accounts for 77% of the hydrogen cyanide produced; by-product of acrylonitrile production accounts for the remaining 23% (CMR 1993; SRI 1995). The methods of commercial production of potassium and sodium cyanide include reacting potassium or sodium carbonate with carbon and ammonia, and reacting hydrogen cyanide with potassium or sodium hydroxide (Curry 1992; HSDB 1996). Sodium cyanide can also be prepared by heating sodium amide with carbon or by melting sodium chloride and calcium cyanamide together in an electric furnace (Hartung 1982). Potassium silver cyanide is manufactured by adding silver chloride to a solution of potassium cyanide (Sax and Lewis 1987). Calcium cyanide is manufactured by heating calcium cyanamide with a source of carbon in electric furnaces at temperatures greater than 1,000 °C (Curry 1992; Homan 1987). It may also be produced by neutralization of lime with hydrogen cyanide (Homan 1987).

Cyanogen is usually prepared by adding an aqueous solution of sodium or potassium cyanide to an aqueous solution of copper sulfate(II) or chloride (Homan 1987; Windholz 1983). It may also be produced by heating mercury cyanide, or by heating hydrogen cyanide in the presence of a catalyst (Homan 1987). Cyanogen chloride is produced by the action of chlorine on hydrogen cyanide or by the action of chlorine on moist sodium cyanide suspended in carbon tetrachloride and kept cooled to -3 °C (Homan 1987; Windholz 1983). Ammonium thiocyanate is produced by boiling an aqueous solution of

Table 4-1. Facilities That Manufacture or Process Hydrogen Cyanide

Facility	Location ^a	Range of maximum amounts on site in pounds	Activities and uses
DEGUSSA CORP.	THEODORE, AL	100,000-999,999	Produce; For on-site use/processing; For sale/distribution; As a reactant
VEBA CORP.	THEODORE, AL	100,000-999,999	As a reactant
ULTRAMAR CORP.	WILMINGTON, CA	0-99	Produce; As an impurity
MITSUBISHI RAYON CO. LTD.	SACRAMENTO, CA	100-999	Produce; As a by-product
PMC INC.	CHICAGO, IL	0-99	Produce; As a by-product
NA	ASHLAND, KY	0-99	Produce; As an impurity
NA	ASHLAND, KY	0-99	Produce; As a by-product; As an impurity
CABOT CORP.	VILLE PLATTE, LA	100-999	Produce; As a by-product
CIBA-GEIGY CORP.	ST. GABRIEL, LA	1,000,000-9,999,999	Produce; For on-site use/processing; As a reactant
DOW CHEMICAL CO.	PLAQUEMINE, LA	1,000-9,999	Produce; As a by-product
NA	WESTWEGO, LA	100,000-999,999	Produce; For on-site use/processing; As a by-product; As a reactant
CABOT CORP.	FRANKLIN, LA	100-999	Produce; As a by-product
KOCH IND. INC.	ROSEMOUNT, MN	100-999	Produce; As a by-product; As an impurity
HAMPSHIRE HOLDINGS CORP.	NH	1,000,000-9,999,999	As a reactant
ARCADIAN CORP.	LIMA, OH	1,000,000-9,999,999	Produce; For sale/distribution; As a by-product
HAMPSHIRE CHEMICAL CORP.	LIMA, OH	1,000-9,999	As a reactant
LONZA INC.	WILLIAMSPORT, PA	100,000-999,999	As a reactant
AMOCO CHEMICAL CO.	PIEDMONT, SC	0-99	Produce; As a by-product
ALBEMARLE CORP.	ORANGEBURG, SC	10,000-99,999	As a reactant
BASF CORP.	ROCK HILL, SC	0-99	Produce; As a by-product
AKZO NOBEL NV	ROCKWOOD, TN	0-99	Produce; As a by-product
E. I. DU PONT DE NEMOURS & CO.	MEMPHIS, TN	1,000,000-9,999,999	Produce; For on-site use/processing; For sale/distribution; As a by-product; As a reactant
ICI AMERICAS INC.	MEMPHIS, TN	1,000-9,999	As a reactant
MONSANTO CO.	ALVIN, TX	100,000-999,999	Produce; Import; For on-site use/processing; As a by-product; As a reactant
DOW CHEMICAL USA	FREEPORT, TX	0-99	Produce; For on-site use/processing; As an impurity; As a reactant

Table 4-1. Facilities That Manufacture or Process Hydrogen Cyanide (continued)

Facility	Location ^a	Range of maximum amounts on site in pounds	Activities and uses
BP AMERICA	PORT LAVACA, TX	100,000-999,999	Produce; For on-site use/processing; As a by-product; As an impurity; As a reactant
NA	TEXAS CITY, TX	10,000-99,999	Produce; For on-site use/processing; As a by-product; As a reactant
CABOT CORP.	PAMPA, TX	0-99	Produce
ROHM & HAAS CO.	DEER PARK, TX	10,000-99,999	Produce; For on-site use/processing; As a reactant
NA	DEER PARK, TX	100,000-999,999	As a reactant
W. R. GRACE & CO.-CONN.	DEER PARK, TX	0-99	As a reactant
ISK ENTERPRISES CORP.	HOUSTON, TX	100-999	Produce; As a by-product
E. I. DU PONT DE NEMOURS & CO.	BEAUMONT, TX	10,000-99,999	Produce; For on-site use/processing; For sale/distribution; As a by-product; As a reactant
ICI ACRYLICS INC.	NEDERLAND, TX	10,000-99,999	As a reactant
E. I. DU PONT DE NEMOURS & CO.	ORANGE, TX	100,000-999,999	Produce; For on-site use/processing; For sale/distribution; As a reactant
E. I. DU PONT DE NEMOURS & CO.	VICTORIA, TX	No Data	Produce; For on-site use/processing; As a reactant
HERCULES INC.	MAGNA, UT	0-99	Produce; As a by-product
MURPHY OIL USA INC.	SUPERIOR, WI	0-99	Produce; As a by-product
CABOT CORP.	WAVERLY, WV	0-99	Produce; As a by-product
FMC CORP.	GREEN RIVER, WY	0-99	Produce; For on-site use/processing; As a reactant

Source: TRI93 1995

^a Post office state abbreviations used

NA = not available

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ammonium cyanide with sulfur or polysulfides or by reaction of ammonia and carbon disulfide (Homan 1987; Sax and Lewis 1987).

4.2 IMPORT/EXPORT

The imports and exports of hydrogen cyanide through principal U.S. customs districts are negligible (CMR 1993). Recent import and export data for some of the cyanide compounds included in this profile are summarized in Table 4-2 (USDOC 1994, 1995). As shown in Table 4-2, over the period January 1990 through December 1993, import volumes for thiocyanates, cyanates, and fulminates increased, whereas import volumes of calcium cyanide, cyanides and cyanide oxides of sodium, other cyanides and cyanide oxides, and non-aromatic thiocyanates used for pesticides decreased markedly. Import volumes for potassium cyanide also decreased during the period January 1990 through December 1992, but it was the only compound listed that increased steadily over the next 2 years. Italy, Germany, and Great Britain were the primary exporters of these cyanide chemicals to the United States (USDOC 1994). The most recent import data that could be found for copper (I) cyanide indicate that 0.52 and 0.26 million pounds of this compound were imported into the United States in 1984 and 1986, respectively (HSDB 1996). Recent import data could not be found in the available literature for potassium silver cyanide, cyanogen, or cyanogen chloride.

Export volumes of cyanide compounds (foreign and domestic volumes combined) shown in Table 4-2 fluctuated widely over the period January 1989 and April 1994. No obvious trends were evident except for potassium cyanide, where export volumes decreased from 3.13 million pounds in 1989 to 0.46 million pounds in 1994. Export data could not be found in the available literature for calcium cyanide, potassium silver cyanide, cyanogen, or cyanogen chloride.

4.3 USE

The predominant users of cyanides are the steel, electroplating, mining, and chemical industries. The principal cyanide compounds used in industrial operations are potassium and sodium cyanide and calcium cyanide, particularly in metal leaching operations (Curry 1992; EPA 1992g). Cyanides have well established uses as insecticides and fumigants; in the extraction of gold and silver ores; in metal cleaning; in the manufacture of synthetic fibers, various plastics, dyes, pigments, and nylon; and as reagents in analytical chemistry (EPA 19928; Towill et al. 1978). Cyanogen has been used as a high-energy fuel in the chemical industry and as a rocket or missile propellant; cyanogen and its halides are used in organic

Table 4-2. Import and Export Volumes of Cyanide Compounds^a

Compounds	Imports (million pounds)						Exports (million pounds)						
	1990	1991	1992	1993	1994	Total ^b	1989	1990	1991	1992	1993	1994	Total ^c
Potassium cyanide	1.59	1.29	1.29	1.55	1.67	7.39	3.13	1.99 ^d	0.21	0.27	0.49	0.46 ^d	6.55
Calcium cyanide	12.01	12.30	1.78	ND ^e	ND	26.09 ^f	ND	ND	ND	ND	ND	ND	
Cyanides and cyanide oxides of sodium	28.14	28.94	10.10	6.77	5.68	79.63	123.3	142.9	104.6	132.9	136.6	150.2 ^d	790.5
Other cyanides and cyanide oxides	0.67	1.49	1.25	1.29	1.21	5.91	1.04	0.94	0.86	0.70	1.50	0.91	5.95
Thiocyanates, cyanates, and fulminates	1.11	1.49	1.85	1.89	1.62	7.96	1.39	0.80	0.72	0.82	0.90	3.07	7.70
Nonaromatic thiocyanates used for pesticides	ND	2.66	2.21	1.30	0.40 ^g	6.57	ND	ND	ND	ND	ND	ND	

^aUSDOC (1994, 1995).^bTotal import volume from January 1990 through December 1994.^cTotal export volume from January 1989 through December 1994.^dValues represent domestic export volumes only.^eND = No data.^fTotal import volume for 1990 through 1992.^gImport volume from January through April 1994

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syntheses, as pesticides and fumigants, and in gold-extraction processes (Towill et al. 1978). When used in pesticidal applications and in accordance with the product label, cyanide compounds are regulated by the EPA under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) (EPA 1992g).

As a commercially available product, hydrogen cyanide is sold as a gas and is also available as a technical grade liquid in concentrations of 5, 10, and 96-99.5%. Almost all grades of hydrogen cyanide contain a stabilizer such as phosphoric acid to prevent decomposition and explosion (Curry 1992). In recent years, the use of hydrogen cyanide in the nylon and methyl methacrylate production processes has produced a strong demand. The use pattern for hydrogen cyanide is the following: adiponitrile (for nylon 6/6), 43%; methyl methacrylate, 32%; sodium cyanide, 10%; cyanuric chloride, 5%; chelating agents, 5%; and miscellaneous uses, including methionine and nitriloacetic acid, 5% (CMR 1993). Miscellaneous applications also include the use of hydrogen cyanide as an insecticide and rodenticide for fumigating enclosed spaces (grain storage, etc.) (Worthing 1987) and its use in the manufacture of ferrocyanides, acrylates, lactic acid, pharmaceutical, and specialty chemicals (Worthing 1987).

Cyanide salts have various uses. The most significant applications of compounds included in this profile are uses in electroplating and metal treatment, as an anti-caking agent in road salts, and in gold and silver extraction from ores. Minor applications include use as insecticides and rodenticides, as chelating agents, and in the manufacture of dyes and pigments (Sax and Lewis 1987; Towill et al. 1978; Worthing 1987). Calcium cyanide is used as a cement stabilizer (Curry 1992; Windholz 1983) and has had limited use in rodent control and as a beehive fumigant (Lowe and Sullivan 1992). Formerly used as a polymerization catalyst and as an antifouling agent in marine paints, copper (I) cyanide continues to be used in plating baths for silver, brass, and copper-tin alloy plating. Many metal polishes contain potassium or sodium cyanide. Potassium cyanide has a primary use in silver plating and is also used as a reagent in analytical chemistry. Potassium and sodium cyanide are used in combination for nitriding steel (HSDB 1996). One method of achieving hardened, weather-resistant metal surfaces uses a process known as cyaniding which involves heating the metal in a liquid solution of sodium cyanide, sodium chloride and sodium carbonate in the presence of atmospheric oxygen (Curry 1992). Fumigation of fruit trees, railway cars, and warehouses, and treatment of rabbit and rat burrows and termite nests are included among the former uses for sodium cyanide (HSDB 1996).

Cyanogen, a colorless gas with an almond-like odor, is used in organic syntheses, as a fumigant, as a fuel gas for welding and cutting heat-resistant metals, and as a rocket and missile propellant with ozone or fluorine (Sax and Lewis 1987; HSDB 1996). Applications of cyanogen chloride include use in chemical

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syntheses, as a military poison gas, as a warning agent in fumigant gases, as a metal cleaner, in ore refining, and in the production of triazine herbicides, optical brighteners, dyestuffs and synthetic rubber (Farm Chemicals Handbook 1994; Hartung 1982; Homan 1987; HSDB 1996; Windholz 1983).

Ammonium thiocyanate is used as an ingredient in antibiotic fermentations, pesticides, liquid rocket propellants, adhesives, and matches; in photographic processes; to improve the strength of silks; in the manufacture of transparent artificial resins; and as a weed killer and defoliant (Sax and Lewis 1987; Windholz 1983).

4.4 DISPOSAL

It has been estimated that 4.7 billion gallons of cyanide-containing wastes and 0.8 billion gallons of reactive wastes containing cyanide compounds were generated in the United States in 1983 (Grosse 1986). Regulations governing the treatment and disposal of cyanide-containing wastes are detailed in Chapter 7. Cyanide is listed among the 65 toxic pollutants regulated by the Effluent Guidelines and Standards given in Title 40, Sections 400-475, of the Code of Federal Regulations. The pretreatment standards established for point source categories such as hydrogen peroxide manufacturing, electroplating, metal finishing, and ferroalloy manufacturing, regulate cyanides as cyanide amenable to chlorination or total cyanide. Under the Resource Conservation and Recovery Act (RCRA), cyanide is listed as a hazardous waste when it is a discarded as a commercial chemical product, off-specification species, container residue, or spill residue (EPA 1980a); a waste from non-specific sources; or a waste from specific sources. Cyanide salts and complexes are the basis for listing 11 solid waste streams as hazardous wastes under RCRA (EPA 1986). According to RCRA, cyanide-containing wastes are required to be treated by the best available technology before the wastes are disposed of in land. Cyanogen- and cyanogen chloride-containing waste, for example, are assigned the hazardous waste codes PO31 and P033, respectively, and must be treated by chemical or electrolytic oxidation employing specific oxidizing reagents (e.g., hypochlorite, peroxides, ozone or ultraviolet light assisted ozone) or other reagents of equivalent efficiency; wet air oxidation incorporating a surrogate or indicator parameter; or treatment by incineration in units operated in compliance with RCRA standards (EPA 1986f). The concentration of cyanide permissible in wastes for land disposal vary according to the nature of wastes. The maximum concentration in treated waste (i.e., non-waste water) should not exceed 590 mg/kg for total cyanides and 30 mg/kg for cyanides amenable to chlorination (EPA 1988c). While liquids are prohibited from land disposal, the maximum concentrations allowable in most treated waste waters, with the exception of the bottom streams from the acetonitrile

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column and the waste water stripper used in the production of acrylonitrile, are 1.9 mg/L for total cyanides and 0.86 mg/kg for cyanides amenable to chlorination (EPA 1988c).

Conducted in the presence of sodium hydroxide or sodium hypochlorite, the chemical oxidation method commonly referred to as alkaline chlorination is the most widely used commercial method for treating cyanide-containing wastes. This method results in the conversion of the cyanide solution to the less toxic cyanate. Depending on the cyanides present, the product will be a sludge or solution, which when sufficient reaction time has been allowed, will largely be devoid of free cyanide (IRPTC 1985). Cyanide salts should not be treated with acid in preparation for disposal or flushed into drains which may contain or subsequently receive acid waste. Acidification is not a recommended method of treatment prior to disposal because of the liberation of hydrogen cyanide. Similarly, incineration of cyanides must proceed with caution and is not recommended unless extensive equipment capable of safely handling liberated hydrogen cyanide is available (IRPTC 1985). Of the cyanide compounds included in this profile, only hydrogen cyanide and cyanogen chloride are listed as potential candidates for rotary kiln incineration or fluidized bed incineration (HSDB 1996).

The biodegradation of cyanides has been investigated, with varying results, for several industrial processes, and additional research in this area is needed. While investigations of the potential for microbial species found in mineral processing waste waters demonstrate effective removal of cyanide, metal complexed cyanide, and thiocyanate (Boucabeille 1994b), complex cyanides did not appear amenable to biodegradation at gasworks sites (Thomas and Lester 1993). Formaldehyde in basic solution can convert free cyanide to substituted acetates. Copper and silver in electroplating wastes can be recovered as free metals with formaldehyde reduction. The complexes of zinc and cadmium can be recovered as the oxides with formaldehyde treatment. Calcium or sodium polysulfide treatment converts some cyanide wastes into less toxic thiocyanate. These examples suggest that typical treatments involve the decomposition of cyanides to less toxic compounds by physical or chemical processes. More than 97% of cyanide is typically removed from waste waters by alkaline chlorination, electrolysis, or ozonation process. Cyanide from some wastes can be removed by ion-exchange resins. After using an appropriate treatment method, cyanide wastes may be disposed of in a secured sanitary landfill (Grosse 1986; Higgins and Desher 1988; Tucker and Carson 1985). The possibility of disposal by injection of high-pH cyanide wastes into sandstone has also been investigated (Scrivner et al. 1986). It appears that in 1992 0.8 million pounds of hydrogen cyanide were disposed of by underground injection (see Section 5.2) (TR193 1995).

